High temperature synchrotron HRPD study on Sr-fresnoite.

A.M.T. Bell¹, H-P. Liermann¹ and C.M.B.Henderson².

1. HASYLAB/DESY, Notkestraße 85, 22607 Hamburg, Germany.
2. SEAES, University of Manchester, Manchester M13 9PL, UK.

The Sr analogue of the mineral fresnoite (Sr₂TiSi₂O₈) is of interest as a potential storage medium for radioactive Sr from nuclear waste [1]. No high-temperature crystal structure information is known for this material. However, ICDD PDF card 39-228 states that at room temperature this material is $P4_{2_1}2_1$ tetragonal with lattice parameters $a = 8.3218(2)\text{Å}$ and $c = 5.0292(2)\text{Å}$. A test experiment was done on a synthetic sample of Sr-fresnoite using the PETRA-III P02.1 high-resolution X-ray powder diffraction beamline. The sample was mounted in a 0.7mm diameter quartz capillary and an initial powder data set was collected at 293K; data were collected out to 11.7°$2\theta$ using a PerkinElmer XRD 1621 flat panel image plate detector. The sample was then heated up to 573K with the Cyberstar hot air gas blower attachment and more powder data were collected. Further data were collected in 50K increments up to 1223K. A synchrotron X-ray wavelength of 0.206678Å was used. Figure 1 shows the experimental setup on P02.1.

Even though the counting time for each powder diffraction data set was only 30s, the very high synchrotron X-ray flux available on P02.1 meant that four phases were identified in the powder data. Sr-fresnoite (81(1)%) was the main phase; SrTiO₃ (7.0(6)%) and SrSiO₃ (7.4(8)%), as well as the CeO₂ internal standard (4.6(3)%), were also found as impurity phases as was the CeO₂ internal standard (4.6(3)%). Four-phase Rietveld [2] refinements were successfully done on these data using FULLPROF [3]. Full structural parameters could only be refined for the Sr-fresnoite phase, not for any of the other minor impurity phases. The crystal structure of fresnoite [4] (Ba₂TiSi₂O₈) was used as an initial structure for Rietveld refinement. Figure 2 (above left) shows a plot of these powder data on heating between 573-1223K. Figure 3 (above right) shows the Rietveld difference plot using the powder data collected at 293K.
Apart from thermal expansion no structural changes were observed in any of the four phases between 293-1223K, the \textit{P4bm} Sr-fresnoite structure is retained. Figure 4 (left) shows changes in lattice parameters on heating. The increase in the tetragonal $c$ lattice parameter is (approximately) linear over the whole temperature range. However, the increase in the tetragonal $a$ lattice parameter is (approximately) linear only between 573-1223K.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{lattice_parameters.png}
\caption{Changes in lattice parameters on heating.}
\end{figure}

**Conclusions**

The new PETRA-III P02.1 HRPD beamline has been used to collect powder diffraction data on a sample of Sr-fresnoite (Sr$_2$TiSi$_2$O$_8$) between 293-1223K, the data collection time at each temperature was only 30s. Full structural parameters could be refined for Sr-fresnoite, the \textit{P4bm} 293K structure is retained up to 1223K.

This test experiment shows that the image plate detector on P02.1 can be used to collect high quality powder diffraction data with short data collection times.

**References**